

AD-A137 263

KINETIC MECHANISMS FOR PREMIXED LAMINAR STEADY STATE  
METHANE/AIR FLAMES..(U) ARMY ARMAMENT RESEARCH AND  
DEVELOPMENT CENTER ABERDEEN PROVIN.. T P COFFEE DEC 83  
ARBRL-TR-02539 SBI-AD-F300 369

1/1

UNCLASSIFIED

F/G 21/2

NL

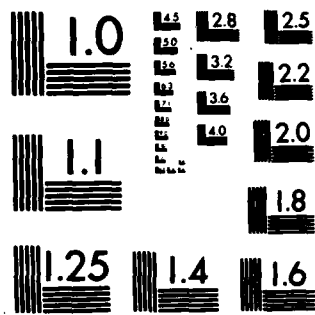
END

DATE

FILED

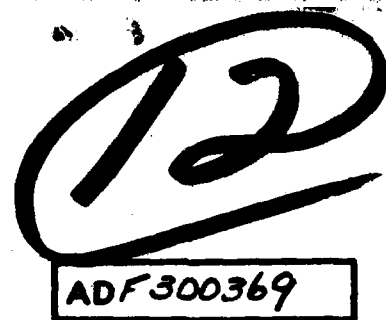
3 84

DTIC



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

AD A 137263



TECHNICAL REPORT ARBRL-TR-02539

KINETIC MECHANISMS FOR PREMIXED, LAMINAR,  
STEADY STATE METHANE/AIR FLAMES

Terence P. Coffee

December 1983



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT CENTER  
**BALLISTIC RESEARCH LABORATORY**  
ABERDEEN PROVING GROUND, MARYLAND

Approved for public release; distribution unlimited.

DTIC FILE COPY

84 01 16 017

DTIC  
ELECTE  
JAN 17 1984  
S D D

Destroy this report when it is no longer needed.  
Do not return it to the originator.

Additional copies of this report may be obtained  
from the National Technical Information Service,  
U. S. Department of Commerce, Springfield, Virginia  
22161.

The findings in this report are not to be construed as  
an official Department of the Army position, unless  
so designated by other authorized documents.

*The use of trade names or manufacturers' names in this report  
does not constitute endorsement of any commercial product.*

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM												
1. REPORT NUMBER <b>TECHNICAL REPORT ARRL-TR-02539</b>	2. GOVT ACCESSION NO. <b>AD-A137 243</b>	3. RECIPIENT'S CATALOG NUMBER												
4. TITLE (and Subtitle)  <b>KINETIC MECHANISMS FOR PREMIXED, LAMINAR, STEADY STATE METHANE/AIR FLAMES</b>		5. TYPE OF REPORT & PERIOD COVERED <b>Final</b>												
7. AUTHOR(s)  <b>Terence P. Coffee</b>		6. PERFORMING ORG. REPORT NUMBER												
9. PERFORMING ORGANIZATION NAME AND ADDRESS <b>US Army Ballistic Research Laboratory, ARDC ATTN: DRSMC-BLI(A) Aberdeen Proving Ground, MD 21005</b>		8. CONTRACT OR GRANT NUMBER(s)												
11. CONTROLLING OFFICE NAME AND ADDRESS <b>US Army AMCCOM, ARDC Ballistic Research Laboratory, ATTN: DRSMC-BLA-S(A) Aberdeen Proving Ground, MD 21005</b>		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS  <b>1L161102AH43</b>												
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE <b>December 1983</b>												
		13. NUMBER OF PAGES <b>41</b>												
		15. SECURITY CLASS. (of this report)  <b>Unclassified</b>												
		16a. DECLASSIFICATION/DOWNGRADING SCHEDULE												
15. DISTRIBUTION STATEMENT (of this Report)  <b>Approved for public release; distribution unlimited.</b>														
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)														
18. SUPPLEMENTARY NOTES														
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) <table border="0"> <tr> <td>Laminar Flames</td> <td>Methane Flames</td> <td>Temperature Profiles</td> </tr> <tr> <td>Premixed Flames</td> <td>Detailed Kinetics</td> <td></td> </tr> <tr> <td>Steady State Flames</td> <td>Burning Velocity</td> <td></td> </tr> <tr> <td>One-Dimensional Flames</td> <td>Species Profiles</td> <td></td> </tr> </table>			Laminar Flames	Methane Flames	Temperature Profiles	Premixed Flames	Detailed Kinetics		Steady State Flames	Burning Velocity		One-Dimensional Flames	Species Profiles	
Laminar Flames	Methane Flames	Temperature Profiles												
Premixed Flames	Detailed Kinetics													
Steady State Flames	Burning Velocity													
One-Dimensional Flames	Species Profiles													
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <b>REF</b> <p>A number of kinetic schemes have been used to model premixed, laminar, one-dimensional methane/air flames. Seven such kinetic schemes, including two new models, are compared with one another and with experimental data. The two new models, one with 14 species and one with 20 species, both agree with the experimental data over a range of stoichiometries from lean to rich.</p> <p>(Continued)</p>														

DD FORM 1 JAN 75 1473

EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. Abstract (Cont'd):

All of the models show good agreement for lean to slightly rich flames. This does not validate any of the models, even for this limited range. Rather, it is shown that the quantities measured are fairly insensitive to much of the mechanism. Therefore, models with incorrect kinetics can agree with the experimental data.

In particular, the contribution of the  $C_2$  species to methane combustion is examined. While these species are important, we conclude that there is insufficient data to determine quantitatively the effects of the  $C_2$  chemistry reactions.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

# TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES.....	5
LIST OF TABLES.....	7
I. INTRODUCTION.....	9
II. NUMERICAL PROCEDURE.....	9
III. KINETIC SCHEME.....	11
IV. COMPARISON WITH EXPERIMENTAL DATA.....	15
V. SENSITIVITY ANALYSIS.....	8
VI. DISCUSSION.....	24
VII. LOW PRESSURE FLAMES.....	29
VIII. CONCLUSIONS.....	30
ACKNOWLEDGEMENT.....	31
REFERENCES.....	32
DISTRIBUTION LIST.....	35

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist.	Avail and/or Special
A/1	



# LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Burning Velocity Versus Equivalence Ratio. Model Values - CF20 (Line), CF14 (Dot), and W23 (Dash). Experimental Points - Andrews and Bradley (Circle), Gunther and Janisch (Triangle), Reed (Plus), and Lindow (Times).....	17
2	Stoichiometric CH <sub>4</sub> /Air Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash). Bechtel Experimental Points. T and OH Profiles.....	19
3	Stoichiometric CH <sub>4</sub> /Air Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash). Bechtel Experimental Points. H <sub>2</sub> and CO Profiles.....	20
4	Stoichiometric CH <sub>4</sub> /Air Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash). Bechtel Experimental Points. O <sub>2</sub> and CH <sub>4</sub> Profiles.....	21
5	Stoichiometric CH <sub>4</sub> /Air Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash). Bechtel Experimental Points. H <sub>2</sub> O and CO <sub>2</sub> Profiles.....	22

# LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Reactions in the $\text{CH}_4/\text{Air}$ System.....	12
2	Logarithmic Sensitivity Coefficients for a Stoichiometric Flame (CF20 Kinetics Scheme).....	23
3	Ratio of CF20 Peak Heights to CF14 Peak Heights as a Function of Equivalence Ratio.....	25
4	Ratio of DL18 Peak Heights to CF20 Peak Heights as a Function of Equivalence Ratio.....	27
5	Ratio of W23 Peak Heights to CF20 Peak Heights as a Function of Equivalence Ratio.....	28
6	A Comparison of Burning Velocities and Peak Mass Fractions for the Low Pressure Flame.....	29
7	Results of the Time Integration of the CF20 Model Profiles. Initial Conditions are Taken at the $\text{CH}_2\text{O}$ Peak.....	30

RESEARCH AND DEVELOPMENT

## I. INTRODUCTION

We are interested here in the detailed kinetics governing premixed, laminar, one-dimensional methane/air flames. The earliest such scheme, introduced by Smoot, Hecker and Williams<sup>1</sup> and by Tsatsaronis,<sup>2</sup> involved 14 species and about 30 reactions. These include the reaction  $\text{CH}_2\text{O} + \text{M} \rightarrow \text{CO} + \text{H}_2 + \text{M}$ , which is probably not an elementary reaction in atmospheric pressure flames. Warnatz<sup>3</sup> introduced a much more complicated scheme involving 23 species and 50 reactions. In particular, he claimed that  $\text{C}_2$  species were important for modeling rich or even near stoichiometric flames. Dixon-Lewis<sup>4</sup> attempted to identify the major reaction channels in large mechanisms such as that of Warnatz. He compares two mechanisms, one with 14 species and one with 18 species (including  $\text{C}_2$  chemistry). Both schemes were considered valid for lean or stoichiometric flames. Dixon-Lewis agrees with Warnatz that it is necessary to include  $\text{C}_2$  chemistry to adequately model rich flames.

In this paper we introduce two new models. The simpler mechanism (14 species, 39 reactions) does not include  $\text{C}_2$  chemistry, but unexpectedly still does a reasonable job of reproducing experimental data for lean and rich flames. The more complicated model (20 species, 63 reactions) is also known to be only an approximation, since a number of species and reactions have been omitted. Nevertheless, it reproduces the experimental data quite well.

Comparisons are made among the seven kinetic models. We conclude that there is insufficient data to validate any particular mechanism at this time.

## II. NUMERICAL PROCEDURE

The governing equations for the chemical species and the temperature are given in Reference 5. These equations are integrated in time, using a finite

---

<sup>1</sup>L.D. Smoot, W.C. Hecker, and G.A. Williams, "Prediction of Propagating Methane-Air Flames," *Combustion and Flame*, Vol. 26, pp. 323-342, 1976.

<sup>2</sup>G. Tsatsaronis, "Prediction of Propagating Laminar Flames in Methane, Oxygen, Nitrogen Mixtures," *Combustion and Flame*, Vol. 33, pp. 217-239, 1978.

<sup>3</sup>J. Warnatz, "The Structure of Laminar Alkane-, Alkene-, and Acetylene Flames," 18th International Combustion Symposium, The Combustion Institute, Pittsburgh, PA, pp. 369-384, 1981.

<sup>4</sup>G. Dixon-Lewis, "Aspects of the Kinetic Modeling of Methane Oxidation in Flames," 1st Specialists Meeting (International) of the Combustion Institute, France, pp. 284-289.

<sup>5</sup>T.P. Coffee and J.M. Heimerl, "Transport Algorithms for Premixed, Laminar Steady-State Flames," *Combustion and Flame*, Vol. 43, pp. 273-289, 1981.

element method, until the steady-state solution is obtained.<sup>6,7,8</sup> All calculations have been done on a Cyber 76.

Besides the kinetics information, thermodynamic and transport data are required. For most species, the polynomial fits of Gordon and McBride<sup>9</sup> are used. For species not included in the above, polynomial fits are made to the data of Benson.<sup>10</sup>

The molecular parameters  $\sigma$ ,  $\epsilon/k$ , and  $\mu$  are from Warnatz.<sup>3</sup> The polarizabilities are from Reid and Sherwood.<sup>11</sup> These are used to compute the individual species thermal conductivities and the binary diffusion coefficients. A test problem was also computed using the transport parameters of Svehla.<sup>12</sup> The results were virtually identical with the previous calculation using the Warnatz parameters.

The multicomponent mass fluxes ( $\rho Y_i V_i$ ) and heat flux ( $q$ ) are computed using the methods of Reference 5. All the preliminary work was done using Method V, the simplest procedure. Convergence took from 2 to 12 minutes of computer time, depending on the mechanism and the stoichiometry. In general, very rich or very lean flames (near the extinction point) took longer to converge. Once a particular problem had been solved using one kinetics set, the steady state solution could be used as the start of the time integration for the other kinetics sets. This led to substantial savings.

---

<sup>6</sup> T.P. Coffee and J.M. Heimerl, "A Method for Computing the Flame Speed for a Laminar, Premixed, One Dimensional Flame," ARBRL-TR-02212, January 1980 (AD A082803).

<sup>7</sup> J.M. Heimerl and T.P. Coffee, "The Detailed Modeling of Premixed, Laminar Steady-State Flames. I. Ozone," Combustion and Flame, Vol. 39, pp. 301-315, 1980.

<sup>8</sup> T.P. Coffee, "A Computer Code for the Solution of the Equations Governing a Laminar, Premixed, One-Dimensional Flame," ARBRL-MR-03165, April 1982.

<sup>9</sup> S. Gordon and B.J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks and Chapman-Jouguet Detonations," NASA-SP-273, 1971 (1981 program version).

<sup>10</sup> S. Benson, Thermochemical Kinetics, 2nd edition, John Wiley and Sons, NY, 1976.

<sup>11</sup> R.C. Reid and J.K. Sherwood, The Properties of Gases and Liquids, 2nd edition, McGraw-Hill, NY, 1966.

<sup>12</sup> R.A. Svehla, "Estimated Viscosities and Thermal Conductivities of Gases at High Temperatures," NASA Technical Report R-132, Lewis Research Center, Cleveland, OH, 1962.

The flame speeds and profiles reported in this paper were computed using transport Method VI. This algorithm is very accurate, but is computationally much more complex. Even using the Method V solutions as starting points, the 14 species model required an additional 30 to 60 minutes of computer time. The 20 species model required an additional 2 to 4 hours.

### III. KINETIC SCHEME

The forward reactions used in this paper are listed in Table 1. The rates of the back reactions are computed from the forward rate coefficients and the equilibrium constant for the reaction. Additional species and reactions were considered, but they turned out to have no noticeable effect on the problems considered.

The first 23 reactions are from Dixon-Lewis. These have been checked extensively in earlier studies of  $H_2/O_2/N_2$  flames<sup>13</sup> and  $CO/H_2/O_2/N_2$  flames.<sup>14</sup>

Reactions 24 through 31 are derived from a series of shock tube experiments by Dean, et al.<sup>15,16</sup> The formaldehyde reaction rates (28 through 31) are substantially lower than the rates previously used in flame modeling.

The CHO reactions (32 through 35) are not well known. We have more or less arbitrarily chosen the values of Dixon-Lewis.<sup>4</sup>

The next four reactions (36 through 39) are a miscellaneous set from a kinetics data base compiled by Gelinas.<sup>17</sup>

These 39 reactions form a 14 species model. Methane is oxidized along the standard pathway  $CH_4 \rightarrow CH_3 \rightarrow CH_2O \rightarrow CHO \rightarrow CO \rightarrow CO_2$ .

For reaction 40, we begin with the high pressure rate  $k = 2.8 \times 10^{14} T^{-0.4}$ . This rate is used by both Warnatz<sup>3</sup> and Dixon-Lewis.<sup>4</sup> It must be

---

<sup>13</sup>G. Dixon-Lewis, "Kinetic Mechanism, Structure, and Properties of Premixed Flames in Hydrogen-Oxygen-Nitrogen Mixtures," Phil. Trans. Roy. Soc. (London), Vol. A292, pp. 45-99, 1979.

<sup>14</sup>M.A. Cherian, P. Rhodes, R.J. Simpson, and G. Dixon-Lewis, "Structure, Chemical Mechanism and Properties of Premixed Flames in Mixtures of Carbon Monoxide, Nitrogen, and Oxygen with Hydrogen and Water Vapor," Phil. Trans. Roy. Soc. (London), Vol. A303, pp. 181-212, 1981.

<sup>15</sup>A.M. Dean, R.L. Johnson, and D.C. Steiner, "Shock-Tube Studies of Formaldehyde Oxidation," Combustion and Flame, Vol. 37, pp. 41-62, 1980.

<sup>16</sup>A.M. Dean and R.L. Johnson, "Shock Tube Studies of the  $N_2O/CH_4/CO/Ar$  and  $N_2O/C_2H_6/CO/Ar$  Systems," Combustion and Flame, Vol. 37, pp. 109-123, 1980.

<sup>17</sup>R.J. Gelinas, "Ignition Kinetics of C1 and C2 Hydrocarbons," Science Applications, Inc., Preprint No. SAI/PL/C279, December 1979.

TABLE 1. REACTIONS IN THE CH<sub>4</sub>/AIR SYSTEM

Reaction	A*	B	C	Reference
1. OH + H <sub>2</sub> → H <sub>2</sub> O + H	1.17E9**	1.3	1825	4
2. H + O <sub>2</sub> → OH + O	1.42E14	0.0	8250	4
3. O + H <sub>2</sub> → OH + H	1.80E10	1.0	4480	4
4. H + O <sub>2</sub> + M' → HO <sub>2</sub> + M'	1.03E18	-0.72	0	4
5. H + HO <sub>2</sub> → OH + OH	1.40E14	0.0	540	4
6. H + HO <sub>2</sub> → O + H <sub>2</sub> O	1.00E13	0.0	540	4
7. H + HO <sub>2</sub> → H <sub>2</sub> + O <sub>2</sub>	1.25E13	0.0	0	4
8. OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	7.50E12	0.0	0	4
9. O + HO <sub>2</sub> → OH + O <sub>2</sub>	1.40E13	0.0	540	4
10. O + HO <sub>2</sub> → OH + O <sub>2</sub>	1.25E12	0.0	0	4
11. H + H + H <sub>2</sub> → H <sub>2</sub> + H <sub>2</sub>	9.20E16	-0.6	0	4
12. H + H + N <sub>2</sub> → H <sub>2</sub> + N <sub>2</sub>	1.00E18	-1.0	0	4
13. H + H + O <sub>2</sub> → H <sub>2</sub> + N <sub>2</sub>	1.00E18	-1.0	0	4
14. H + H + H <sub>2</sub> O → H <sub>2</sub> + O <sub>2</sub>	6.00E19	-1.25	0	4
15. H + H + CO → H <sub>2</sub> + CO	1.00E18	-1.0	0	4
16. H + H + CO <sub>2</sub> → H <sub>2</sub> + CO <sub>2</sub>	5.49E20	-2.0	0	4
17. H + H + CH <sub>4</sub> → H <sub>2</sub> + CH <sub>4</sub>	5.49E20	-2.0	0	4
18. H + OH + M'' → H <sub>2</sub> O + M''	1.60E22	-2.0	0	4
19. H + O + M'' → OH + M''	6.20E16	-0.6	0	4
20. OH + OH → O + H <sub>2</sub> O	5.75E12	0.0	390	4
21. OH + CO → CO <sub>2</sub> + H	1.50E7	1.3	-385	4
22. O + CO + M' → CO <sub>2</sub> + M'	5.40E15	0.0	2300	4

\* A is in units of cm<sup>3</sup>/mole-sec or cm<sup>6</sup>/mole<sup>2</sup>-sec,  $k=AT^B \exp(-C/T)$ .

\*\* 1.17E9 = 1.17 × 10<sup>9</sup>.

23.	$\text{H} + \text{CO} + \text{M}' \rightarrow \text{CHO} + \text{M}'$	5.00E14	0.0	755	4
24.	$\text{CH}_4 + \text{O} \rightarrow \text{CH}_3 + \text{OH}$	4.07E14	0.0	7040	15
25.	$\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$	7.24E14	0.0	7590	15
26.	$\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	1.55E6	2.13	1230	15
27.	$\text{CH}_4 + \text{M} \rightarrow \text{CH}_3 + \text{H} + \text{M}$	4.68E17	0.0	46910	15
28.	$\text{CH}_3 + \text{O} \rightarrow \text{CH}_2\text{O} + \text{H}$	6.02E13	0.0	0	15
29.	$\text{CH}_2\text{O} + \text{O} \rightarrow \text{CHO} + \text{OH}$	1.82E13	0.0	1550	15
30.	$\text{CH}_2\text{O} + \text{H} \rightarrow \text{CHO} + \text{H}_2$	3.31E14	0.0	5290	15
31.	$\text{CH}_2\text{O} + \text{OH} \rightarrow \text{CHO} + \text{H}_2\text{O}$	7.58E12	0.0	72	15
32.	$\text{CHO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	3.00E12	0.0	0	4
33.	$\text{CHO} + \text{H} \rightarrow \text{CO} + \text{H}_2$	4.00E13	0.0	0	4
34.	$\text{CHO} + \text{OH} \rightarrow \text{CO} + \text{H}_2\text{O}$	5.00E12	0.0	0	4
35.	$\text{CHO} + \text{O} \rightarrow \text{CO} + \text{OH}$	1.00E13	0.0	0	4
36.	$\text{CH}_2\text{O} + \text{CH}_3 \rightarrow \text{CHO} + \text{CH}_4$	2.23E13	0.0	2590	16
37.	$\text{CH}_3 + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$	3.98E12	0.0	0	16
38.	$\text{CH}_3 + \text{HO}_2 \rightarrow \text{CH}_4 + \text{O}_2$	1.02E12	0.0	200	16
39.	$\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{OH}$	1.50E14	0.0	11900	16
40.	$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	4.56E37	-7.65	4250	4,17
41.	$\text{C}_2\text{H}_6 + \text{O} \rightarrow \text{C}_2\text{H}_5 + \text{OH}$	2.51E13	0.0	3200	16
42.	$\text{C}_2\text{H}_6 + \text{H} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2$	5.00E2	3.5	2620	16
43.	$\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{C}_2\text{H}_5 + \text{H}_2\text{O}$	6.63E13	0.0	675	16
44.	$\text{C}_2\text{H}_5 + \text{H} \rightarrow \text{C}_2\text{H}_6$	7.23E13	0.0	0	16
45.	$\text{C}_2\text{H}_5 + \text{H} \rightarrow \text{CH}_3 + \text{CH}_3$	3.73E13	0.0	0	16
46.	$\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	2.29E11	0.0	19120	16
47.	$\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$	1.53E12	0.0	2446	16
48.	$\text{C}_2\text{H}_4 + \text{O} \rightarrow \text{CH}_2 + \text{CH}_2\text{O}$	2.53E13	0.0	2516	16
49.	$\text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{CH}_2\text{O} + \text{CH}_3$	5.00E13	0.0	3020	16

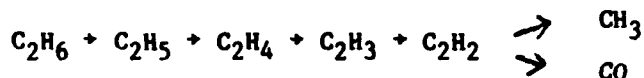
50.	$C_2H_4 + O \rightleftharpoons C_2H_3 + OH$	2.53E13	0.0	2516	16
51.	$C_2H_4 + O_2 \rightleftharpoons C_2H_3 + HO_2$	1.33E15	0.0	27680	16
52.	$C_2H_4 + H \rightleftharpoons C_2H_3 + H_2$	2.00E15	0.0	10000	16
53.	$C_2H_4 + OH \rightleftharpoons C_2H_3 + H_2O$	4.40E14	0.0	3270	16
54.	$C_2H_3 + M \rightleftharpoons C_2H_2 + H + M$	3.01E16	0.0	20380	16
55.	$C_2H_3 + O_2 \rightleftharpoons C_2H_2 + HO_2$	1.57E13	0.0	5030	16
56.	$C_2H_3 + H \rightleftharpoons C_2H_2 + H_2$	7.53E13	0.0	0	16
57.	$C_2H_3 + OH \rightleftharpoons C_2H_2 + H_2O$	1.00E13	0.0	0	16
58.	$C_2H_2 + OH \rightleftharpoons CH_3 + CO$	5.48E13	0.0	6890	16
59.	$CH_3 + H \rightleftharpoons CH_2 + H_2$	2.00E11	0.7	-1500	16
60.	$CH_3 + OH \rightleftharpoons CH_2 + H_2O$	6.00E10	0.7	1010	16
61.	$CH_2 + O_2 \rightleftharpoons CHO + OH$	1.00E14	0.0	1860	16
62.	$CH_2 + O_2 \rightleftharpoons CH_2O + O$	1.00E14	0.0	1860	16
63.	$CH_2 + O_2 \rightleftharpoons CO_2 + H_2$	1.00E14	0.0	1860	16

[M] = total concentration

[M'] =  $[H_2] + 0.74 [CO] + 1.47 [CO_2] + 0.35 [O_2] + 6.5 [H_2O] + 0.44 [N_2]$

[M''] =  $[H_2] + [CO] + [CO_2] + [O_2] + 5.0 [H_2O] + [N_2]$

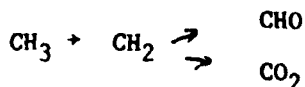
further modified by the fall off method of Luther and Troe.<sup>18</sup> The parameters in Table 1 are a least squares fit of the modified values for a pressure of one atmosphere. This is the primary channel for the formation of C<sub>2</sub> hydrocarbons. The C<sub>2</sub> reactions are 40 through 58.<sup>17</sup> The primary pathway is



There is also a side channel through reactions 48 and 49,



The last five reactions (59 through 63) consist of CH<sub>2</sub> chemistry.<sup>17</sup> The pathway is



This sequence has not been included in previous CH<sub>4</sub>/air flame models.

#### IV. COMPARISON WITH EXPERIMENTAL DATA

Here we compare the seven models discussed above with experimental data. All flames considered in this section are atmospheric pressure, unbounded, methane/air flames with an initial temperature of 298K.

Many measurements have been made on the burning velocity of methane/air flames. Andrews and Bradley<sup>19</sup> have critically reviewed the different experimental techniques. Following their recommendations, we have used the

---

<sup>18</sup>K. Luther and J. Troe, "Weak Collision Effects in Dissociation Reactions at High Temperatures," 17th International Combustion Symposium, The Combustion Institute, Pittsburgh, PA, pp. 535-542, 1979.

<sup>19</sup>G.E. Andrews and D. Bradley, "Determination of Burning Velocities: A Critical Review," *Combustion and Flame*, Vol. 18, pp. 133-153, 1972.

results of four experiments.<sup>20-23</sup> While there is scatter in the data, the results are generally consistent.

The models of Smoot, Hecker and Williams (SHW14) and Dixon-Lewis (DL14 and DL18) are accurate for lean to slightly rich flames. Tsatsaronis [TS14] modified the model of Smoot, et al, so that it is accurate for rich flames, but the calculated burning velocities are low for stoichiometric to slightly lean flames. The more complicated model of Warnatz (W23) is reasonably accurate over the entire range, although the flame speeds are low for rich flames.

Figure 1 shows the results for the two new models introduced in this paper (CF14 and CF20), the model of Warnatz, and the experimental burning velocities. The results are given in terms of the equivalence ratio  $\phi = 2 XCH_4/XO_2$ , where X represents the initial mole fraction of the species. All experimental values have been corrected to 298 K. Both new models are accurate over the entire range, although slightly low for very lean or very rich flames. The values calculated here using the Warnatz model (W23) for rich flames are slightly lower than those reported by Warnatz.<sup>3</sup> We do not know the reason for the discrepancy.

Laser methods have recently been used to measure species and temperature profiles. Bechtel and Teets<sup>24</sup> measured OH profiles using laser-induced fluorescence for  $\phi = 0.86, 1.00$ , and  $1.25$ . In a later paper, Bechtel, et al,<sup>25</sup> measured  $H_2$ , CO,  $CH_4$ ,  $O_2$ ,  $CO_2$ ,  $H_2O$ , and temperature profiles for the same three cases.

These profiles were compared with calculations using the SHW14 model. Agreement was very good except for the  $H_2$  profile. The measured  $H_2$

---

<sup>20</sup>G.E. Andrews and D. Bradley, "Determination of Burning Velocity by Double Ignition in a Closed Vessel," Combustion and Flame, Vol. 20, pp. 77-89, 1973.

<sup>21</sup>R. Gunther and G. Janish, "Measurements of Burning Velocity in a Flat Flame Front," Combustion and Flame, Vol. 19, pp. 49-53, 1972.

<sup>22</sup>R. Lindow, "Eine verbesserte Brennermethode zur Bestimmung der laminaren Flammgeschwindigkeiten von Brenngas/Luft-Gemischen," Brennstoff Wärme Kraft, Vol. 20, pp. 8-14, 1968.

<sup>23</sup>S.B. Reed, J. Mineur, and J.P. McNaughton, "The Effect on the Burning Velocity of Methane of Vitiating of Combustion Air," J. Inst. Fuel, Vol. 44, pp. 149-155, 1971.

<sup>24</sup>J.H. Bechtel and R.E. Teets, "Hydroxyl and Its Concentration Profile in Methane-Air Flames," Applied Optics, Vol. 18, pp. 4138-4144, 1979.

<sup>25</sup>J.H. Bechtel, R.J. Blint, C.J. Dasch, and D.A. Weinberger, "Atmospheric Pressure Premixed Hydrocarbon-Air Flames: Theory and Experiment," Combustion and Flame, Vol. 42, pp. 197-213, 1981.

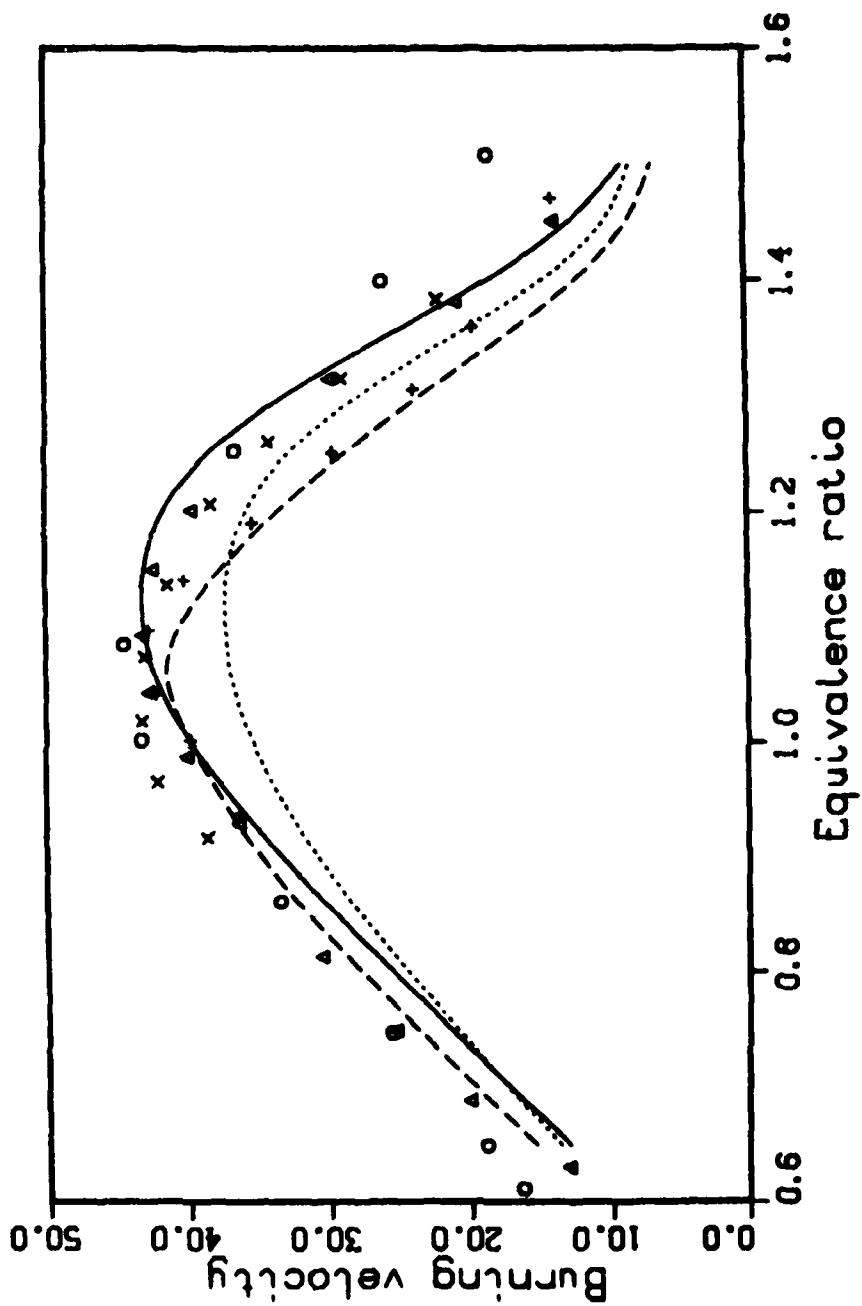


Figure 1. Burning Velocity Versus Equivalence Ratio. Model Values - CF20 (line), CF14 (Dot), and W23 (Dash). Experimental Points - Andrews and Bradley (Circle), Gunther and Janisch (Triangle), Reed (Plus), and Lindow (Times).

concentration was much greater than the calculated  $H_2$  concentration in the leading edge of the flame.

One explanation considered by the authors is an inadequate treatment of the diffusion of  $H_2$  in their model. This appears to be the case. When the SHW14 model was run using our code, agreement for the  $H_2$  profile was very good.

Calculations were made for each of the three cases above for all seven kinetic models. Agreement was excellent for all models for the  $CO_2$ ,  $O_2$ ,  $CH_4$ ,  $H_2O$ , and temperature profiles. The primary difference was that the experimental temperature dropped in the post-flame region, while the model temperatures increased. This can be explained by heat lost to the wall.<sup>25</sup>

Agreement for the  $H_2$  and CO profiles was very good, but with some scatter in the calculated peak heights.

Agreement for the OH profile was good for the lean and stoichiometric cases. For the rich flame, all of the models predicted a higher and earlier peak than that given by the experiment. This suggests either a problem with the experiment or some basic inadequacy in the standard models for rich flames or both.

Figures 2-5 show the experimental profiles for a stoichiometric flame compared to the 3 models including  $C_2$  chemistry. The other models are quite similar.

## V. SENSITIVITY ANALYSIS

A sensitivity analysis is useful in trying to understand a complex system like the  $CH_4$ /air kinetics. A procedure for finding sensitivity coefficients for flames was developed in Reference 26.

This analysis was done for a stoichiometric  $CH_4$ /air flame using the CF20 model. The larger logarithmic sensitivity coefficients  $S_E^i$  for the flame speed are given in Table 2. These are defined such that if the rate of the reaction is changed by a small factor  $\alpha$ , the flame speed will change by  $\alpha$  to the  $S_E^i$  power, i.e.,  $v \equiv v_0 \alpha^{S_E^i}$ . Analytically, the sum of  $S_E^i$  must equal 0.526<sup>26</sup>

The flame is most sensitive to the chain branching reaction 2 [ $H + O_2 \rightarrow OH + H$ ]. Radicals must be produced for the flame to propagate, and reaction 2 is the principal bottleneck for reaction production.

The flame is much less sensitive to the corresponding chain branching reaction 3 [ $O + H_2 \rightarrow OH + H$ ]. Since the  $H_2$  concentration is small, this

---

<sup>26</sup>T.P. Coffey and J.M. Heimerl, "Sensitivity Analysis for Premixed Laminar, Steady-State Flames," Combustion and Flame, Vol. 50, pp. 323-340, 1983.

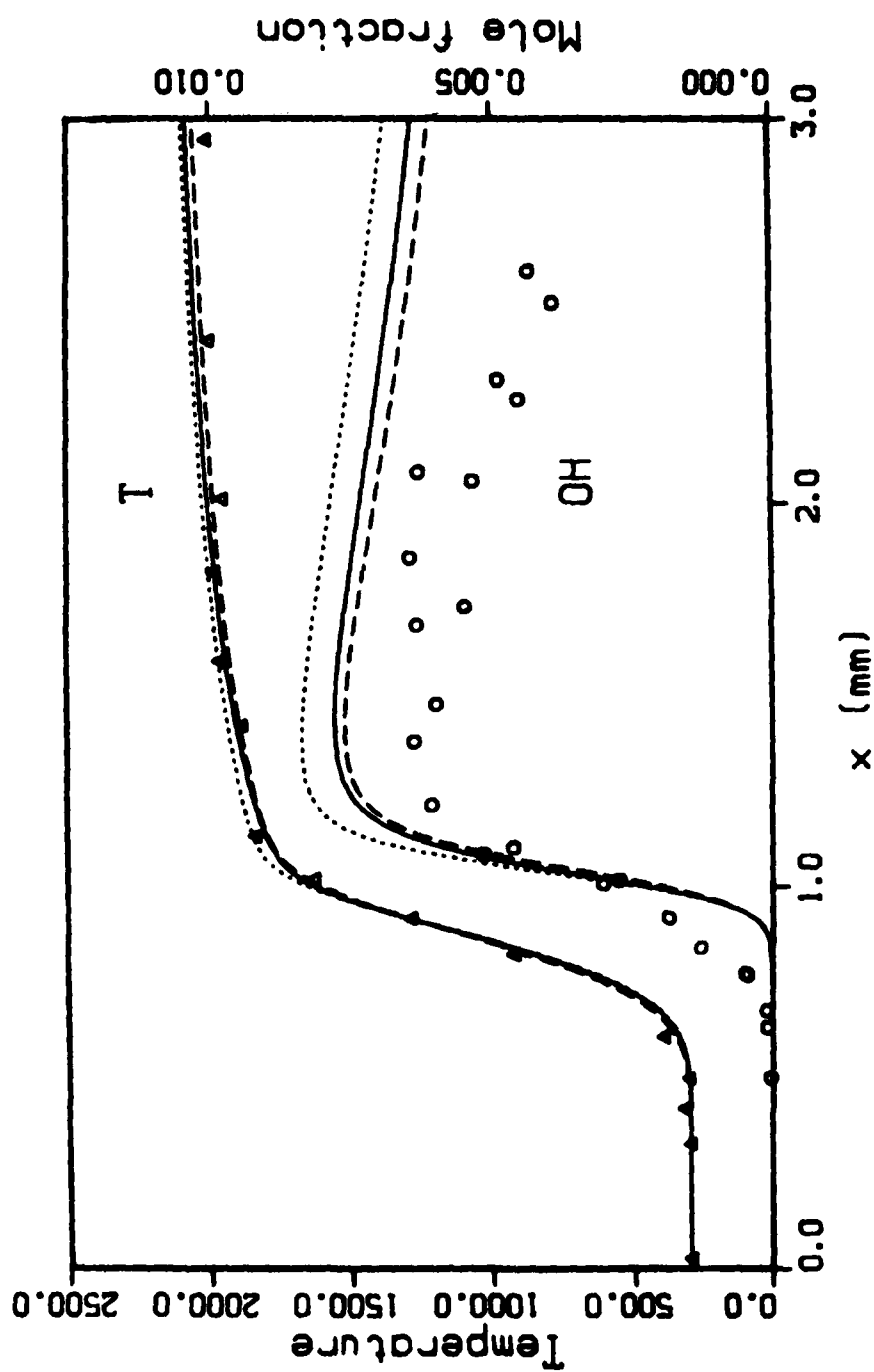


Figure 2. Stoichiometric  $\text{CH}_4/\text{Air}$  Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash). Bechtel Experimental Points. T and OH Profiles.

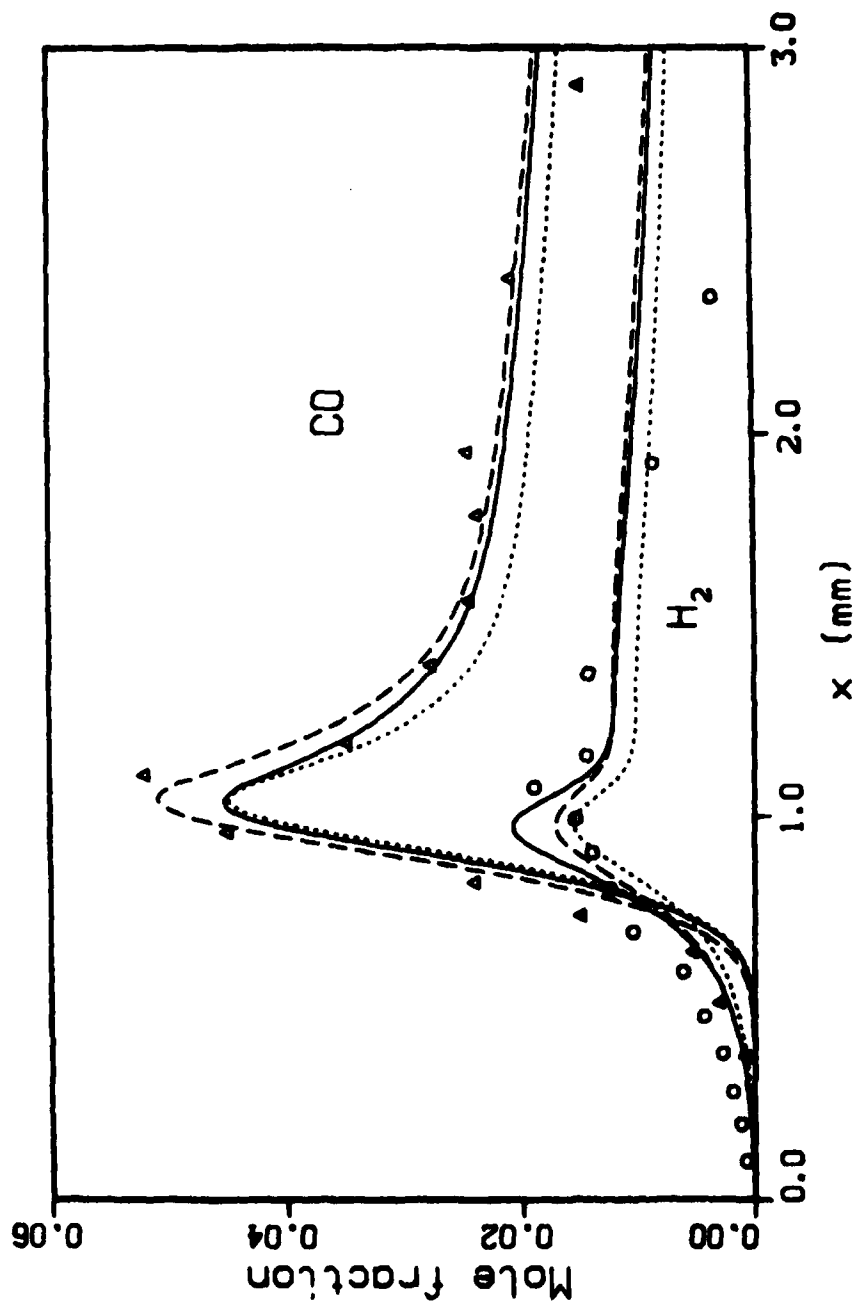


Figure 3. Stoichiometric  $\text{CH}_4/\text{Air}$  Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash).  
Bechtel Experimental Points.  $\text{H}_2$  and CO Profiles.

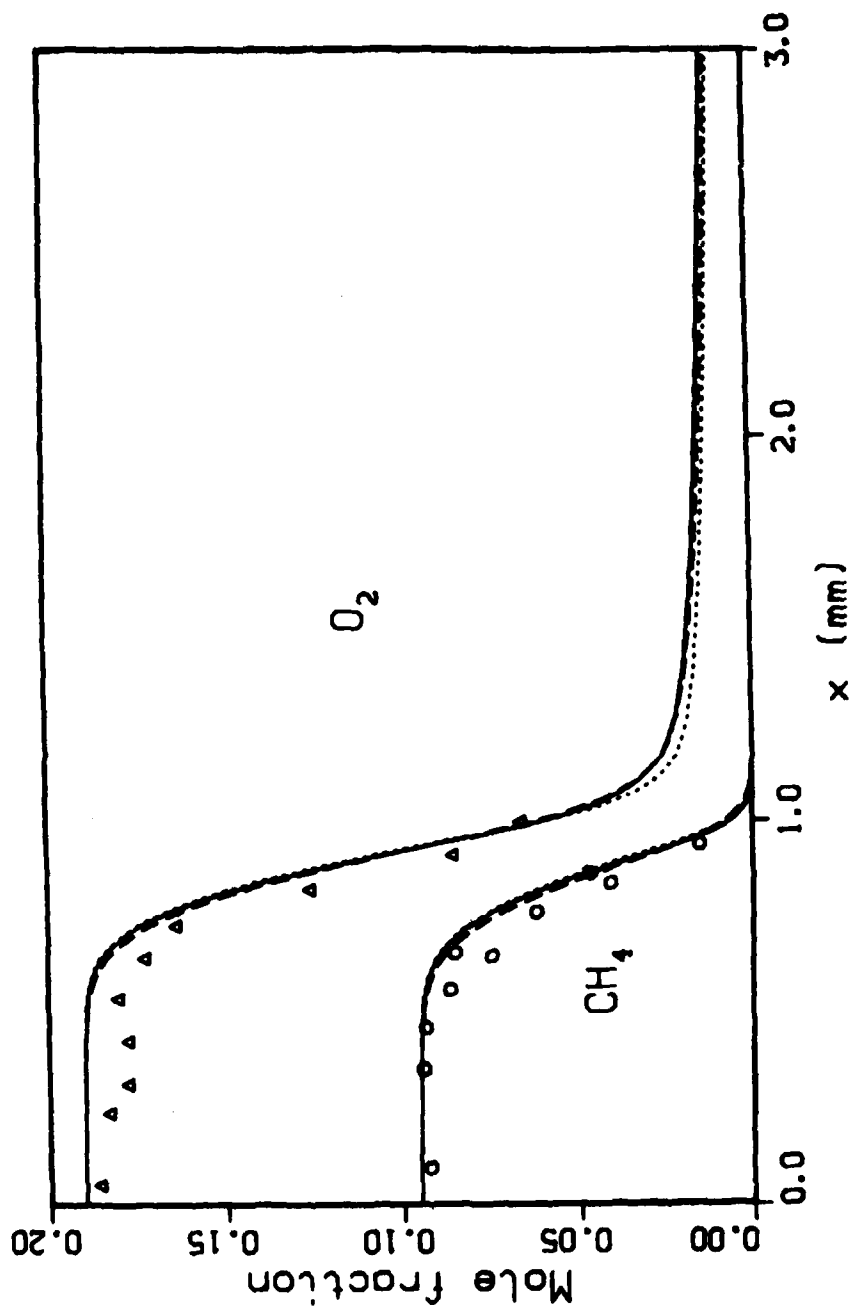


Figure 4. Stoichiometric  $\text{CH}_4/\text{Air}$  Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash).  
Rechtel Experimental Points.  $\text{O}_2$  and  $\text{CH}_4$  Profiles.

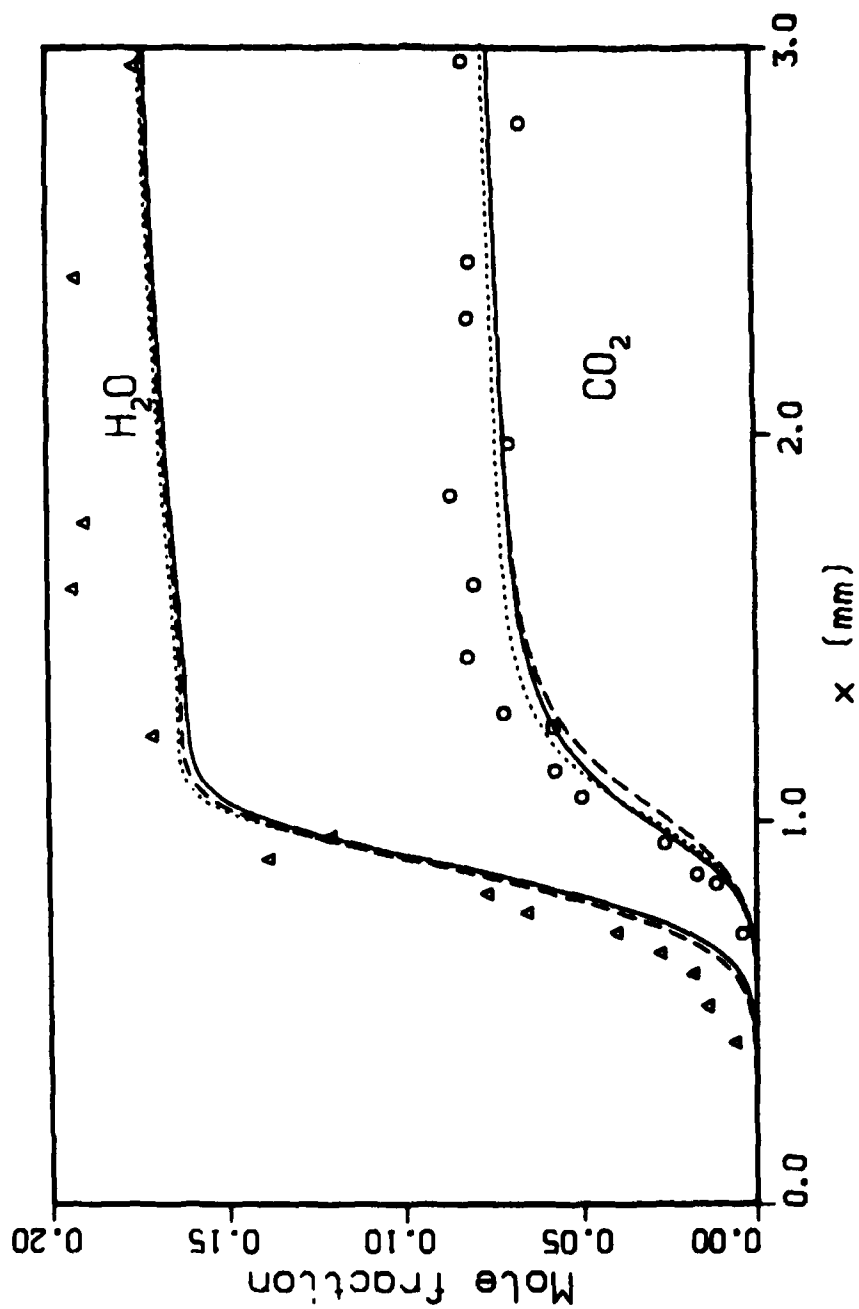


Figure 5. Stoichiometric  $\text{CH}_4/\text{Air}$  Flame. Model Values - CF20 (Line), W23 (Dot), and DL18 (Dash). Bechtel Experimental Points.  $\text{H}_2\text{O}$  and  $\text{CO}_2$  Profiles.

TABLE 2. LOGARITHMIC SENSITIVITY COEFFICIENTS FOR A  
STOICHIOMETRIC FLAME (CF20 KINETICS SCHEME)

Reaction	$S_E^J$	Reaction	$S_E^J$
1	.06	40	-.05
2	.45	59	.09
3	.04	60	.03
4	-.15	61	.03
18	-.05	62	.03
21	.16	63	-.06
23	.07		
25	-.06		
27	-.06		
28	.03		
33	-.04		

reaction is relatively unimportant. Most of the H atoms are generated by other reactions.

Much of the sensitivity analysis can be explained in terms of a shortage of H atoms. Reactions that consume H atoms [4, 18, 25, 27, 33] tend to slow down the flame. Reactions that produce H atoms [1, 3, 21, 23, 28] increase the flame speed. The flame is much more sensitive to the radicals than to the rate at which the intermediates [CH<sub>3</sub>, CH<sub>2</sub>O, CHO, CO] are formed.

Reaction 40 [CH<sub>3</sub> + CH<sub>3</sub> → C<sub>2</sub>H<sub>6</sub>] slows down the flame because it leads to the slower C<sub>2</sub> pathway. However, only about 10% of the CH<sub>3</sub> formed goes to C<sub>2</sub>H<sub>6</sub>. All the other C<sub>2</sub> chemistry rates have very small sensitivity coefficients. For other kinetic schemes, more CH<sub>3</sub> may be converted to C<sub>2</sub>H<sub>6</sub>, and the C<sub>2</sub> reactions would be more important.

Finally, reactions 59 [CH<sub>3</sub> + H → CH<sub>2</sub> + H<sub>2</sub>] and 60 [CH<sub>3</sub> + OH → CH<sub>2</sub> + H<sub>2</sub>O] have positive sensitivity coefficients, even though radicals are consumed. This is because CH<sub>2</sub> reacts rapidly with O<sub>2</sub> to produce radicals through reactions 61 and 62. The corresponding reaction 63, which does not produce radicals, has a negative sensitivity coefficient.

In summary, the flame speed is most sensitive to the production of radicals. The  $H_2/O_2/N_2$  kinetics is the most important for determining the flame speed. The next most important group is the CO to  $CO_2$  chemistry (reactions 21 and 22). In contrast, the flame is fairly insensitive to the specific hydrocarbon reactions.

The  $C_2$  chemistry (reactions 40 to 58) tends to slow down the flame, while the  $CH_3$  to  $CH_2$  chemistry (reactions 59 to 63) increases the burning velocity. The latter reactions are not standard for  $CH_4$  chemistry models. But if these reactions are omitted, the burning velocity is too low, especially for rich flames. So these reactions are important for the CF20 mechanism. Whether these reactions are actually important in  $CH_4$  combustion is yet to be determined.

Sensitivity coefficients for the species and temperature profiles were also computed (as a function of position). The major species ( $CH_4$ ,  $O_2$ ,  $CO_2$ ,  $H_2O$ ) were the least sensitive to changes in the rate coefficients. Next comes the intermediate CO and  $H_2$  and the OH radical. The other radicals ( $H$ ,  $O$ ,  $HO_2$ ) were somewhat more sensitive. The intermediates along the main oxidation pathway ( $CH_3$ ,  $CH_2O$ ,  $CHO$ ) were quite sensitive. The species most affected by rate changes were the  $C_2$  species and  $CH_2$ .

Moreover, the species  $CH_4$ ,  $O_2$ ,  $CO_2$ ,  $H_2O$ , CO,  $H_2$ , OH, H, and O are most sensitive to the rate constants 2 and 4. It is the species along the main oxidation pathway ( $CH_3$ ,  $CH_2O$ , and  $CHO$ ) that are sensitive to the hydrocarbon reactions.

This explains why all the models are in very good agreement with the profiles measured by Bechtel. The profiles measured are the least sensitive profiles, and in any case, are primarily sensitive to changes in the  $H_2/O_2$  subset. A wide range of hydrocarbon reactions and rates can be assumed, as long as an appropriate pathway exists from  $CH_4$  to CO to  $CO_2$  and the flame speed is reasonable.

## VI. DISCUSSION

There is substantial agreement among the models for the profiles measured by Bechtel, et al. It is also useful to see for what profiles the models differ. Experimental measurements of such profiles could help determine which, if any, of the models are correct.

To help analyze the results, a screening analysis is performed.<sup>17</sup> That is, the rate of production and loss for each species as a function of position is partitioned according to the contribution of each reaction. This shows the pathways by which the various species are produced and consumed in the given network. Screening analysis complements a sensitivity analysis, which shows how rate changes can effect the given network.

First, we consider the importance of the  $C_2$  and  $CH_2$  chemistry. Table 3 gives the ratios of the peak mole fractions of the CF20 and CF14 models as a function of stoichiometry, as well as the flame speeds  $S$ . The major species

TABLE 3. RATIO OF CF20 PEAK HEIGHTS TO CF14 PEAK HEIGHTS AS A FUNCTION OF EQUIVALENCE RATIO

	<u>0.65</u>	<u>0.86</u>	<u>1.00</u>	<u>1.25</u>	<u>1.40</u>	<u>1.50</u>
H	.86	.94	.95	.91	1.15	1.33
OH	.98	1.00	1.00	.96	1.14	1.06
O	.92	.96	.96	.92	1.86	1.87
HO <sub>2</sub>	1.57	1.41	1.42	1.70	2.20	1.81
CH <sub>3</sub>	.53	.52	.49	.42	.41	.31
CH <sub>2</sub> O	.89	.99	1.07	1.23	1.51	1.59
CHO	.80	.93	1.00	1.09	1.39	1.09
H <sub>2</sub>	.94	1.02	1.04	1.05	1.02	1.04
CO	.88	.92	.92	.91	.94	1.01
S	.95	1.07	1.12	1.17	1.26	1.07

(CH<sub>4</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O) and the temperature are not included as the profiles are virtually identical. The exception is the rich flames ( $\phi = 1.40$  or  $\phi = 1.50$ ), where the CO<sub>2</sub> profiles show slight differences.

For lean to slightly rich flames, only the CH<sub>3</sub> and HO<sub>2</sub> profiles show large differences. The CF20 model has less CH<sub>3</sub> since the CH<sub>3</sub> + C<sub>2</sub>H<sub>6</sub> and CH<sub>3</sub> + CH<sub>2</sub> reactions deplete this species. The C<sub>2</sub> chemistry then leads to more HO<sub>2</sub> through the reactions 48 [C<sub>2</sub>H<sub>5</sub> + O<sub>2</sub> + C<sub>2</sub>H<sub>4</sub> + HO<sub>2</sub>] and 56 [C<sub>2</sub>H<sub>3</sub> + O<sub>2</sub> + C<sub>2</sub>H<sub>2</sub> + HO<sub>2</sub>].

The similarities between the two models are due to competing effects. The C<sub>2</sub> chemistry tends to slow down the flame. The bulk of the C<sub>2</sub>H<sub>6</sub> formed slowly oxidizes to C<sub>2</sub>H<sub>2</sub>, and then goes to CO through reaction 58 [C<sub>2</sub>H<sub>2</sub> + OH + CH<sub>3</sub> + CO]. The concentrations of the radicals and the intermediates CH<sub>2</sub>O and CHO are all lowered.

The CH<sub>2</sub> chemistry tends to increase the flame speed. Once the CH<sub>2</sub> forms, it oxidizes fairly rapidly by the reactions 61 [CH<sub>2</sub> + O<sub>2</sub> + CHO + OH], 62 [CH<sub>2</sub> + O<sub>2</sub> + CH<sub>2</sub>O + O] and 63 [CH<sub>2</sub> + O<sub>2</sub> + CO<sub>2</sub> + H<sub>2</sub>]. The intermediates CH<sub>2</sub>O and CHO are increased. The radical concentrations are not greatly affected, although the O atom peak does increase.

For the rich flames, more of the CH<sub>3</sub> goes to C<sub>2</sub>H<sub>6</sub> (up to 20%) and also to CH<sub>2</sub> (up to 35%). This leads to slightly higher flame speeds for the CF20 model. The CH<sub>3</sub> peak becomes much smaller. The O and CH<sub>2</sub>O concentrations are substantially higher, due to reaction 62 [CH<sub>2</sub> + O<sub>2</sub> + CH<sub>2</sub>O + O].

The  $H_2$  profile shows relatively minor differences. For the CF14 model, the  $H_2$  is primarily produced through reactions 25 [ $CH_4 + H \rightarrow CH_3 + H_2$ ] and 30 [ $CH_2O + H \rightarrow CHO + H_2$ ]. For the CF20 model, less  $H_2$  is produced through these reactions, but this is compensated for by reactions 59 [ $CH_3 + H \rightarrow CH_2 + H_2$ ] and 42 [ $C_2H_6 + H \rightarrow C_2H_5 + H_2$ ]. The overall rate of production through the various pathways is about the same. As long as the flame speeds are similar, this will be the case.

Similarly, a decrease in the CO production reaction 23 [ $CHO + M' \rightarrow H + CO + M'$ ] is compensated for by reaction 58 [ $C_2H_2 + OH \rightarrow CH_3 + CO$ ].

Next, we consider comparisons among the three models with  $C_2$  chemistry. To conserve computer time, the solutions are generated using the simplest transport algorithm, Method v.<sup>5</sup> Tables 4 and 5 show the ratios of the peak mole fractions and flame speeds. Again, the major species and temperature profiles are virtually identical.

The flame speeds generated by the DL18 model agree with those reported by Dixon-Lewis.<sup>4</sup> The flame speeds generated by the W23 model are lower than those reported by Warnatz (5%-15%).

For the DL18 model, results are not given for  $\phi = 1.50$ . No steady state solution could be generated, as the computed flame always went out.

For lean to slightly rich flames, all three models agree for the temperature and major species profiles. Lower flame speeds are predicted for  $\phi = 1.40$  (DL18 and W23 models) and for  $\phi = 1.50$  (W23 model). At these lower speeds, the flame front is spread out and noticeable differences appear in the profiles.

The H, OH, and O profiles are similar for lean to stoichiometric flames. For rich flames, where the models predict lower flame speeds, the radical concentrations tend to be lower (up to a factor of 2). This is reasonable since large amounts of radicals lead to rapid combustion.

There are large differences in the intermediates  $CH_3$ ,  $CH_2O$ , and  $CHO$ .  $CHO$  is especially variable because of its low concentration. The  $C_2$  species show relatively low concentrations and large variation. But the  $H_2$  and CO profiles, which have larger concentrations, remain similar throughout.

TABLE 4. RATIO OF DL18 PEAK HEIGHTS TO CF20 PEAK HEIGHTS AS A FUNCTION OF EQUIVALENCE RATIO

	<u>0.65</u>	<u>0.86</u>	<u>1.00</u>	<u>1.25</u>	<u>1.40</u>
H	.93	.98	.99	1.01	.38
OH	.98	1.00	1.00	1.01	.50
O	.96	1.00	1.00	.91	.23
HO <sub>2</sub>	.54	.70	.79	.78	.40
C <sub>2</sub> H <sub>6</sub>	3.35	3.53	3.31	2.26	1.10
C <sub>2</sub> H <sub>5</sub>	.23	.51	.77	1.08	1.21
C <sub>2</sub> H <sub>4</sub>	.84	1.71	2.80	3.62	2.30
CH <sub>3</sub>	1.35	1.53	1.62	1.74	1.49
CH <sub>2</sub> O	.62	.64	.69	.97	1.35
CHO	2.16	2.24	2.11	1.95	.81
H <sub>2</sub>	.79	.82	.83	.87	.88
CO	1.15	1.14	1.12	1.10	.97
S	1.00	1.00	.96	.88	.50

TABLE 5. RATIO OF W23 PEAK HEIGHTS TO CF20 PEAK HEIGHTS AS A FUNCTION OF EQUIVALENCE RATIO

	<u>0.65</u>	<u>0.86</u>	<u>1.00</u>	<u>1.25</u>	<u>1.40</u>	<u>1.50</u>
H	1.12	1.01	.97	.71	.64	1.21
OH	1.10	1.09	1.06	.70	.56	.91
O	1.28	1.20	1.11	.48	.51	.71
HO <sub>2</sub>	.74	.92	1.04	.97	.52	.32
CH <sub>2</sub>	.38	.48	.62	.89	.91	1.45
C <sub>2</sub> H <sub>6</sub>	2.68	2.07	1.87	1.66	1.66	1.71
C <sub>2</sub> H <sub>5</sub>	.62	.75	.80	.39	.07	.06
C <sub>2</sub> H <sub>4</sub>	2.23	2.72	4.08	5.40	3.74	3.00
C <sub>2</sub> H <sub>3</sub>	2.64	5.44	9.05	10.56	8.59	9.66
C <sub>2</sub> H <sub>2</sub>	.07	.21	.46	1.20	1.35	1.12
CH <sub>3</sub>	1.42	1.49	1.56	1.40	1.20	1.18
CH <sub>2</sub> O	.41	.47	.52	.59	.76	.99
CHO	.51	.42	.35	.19	.16	.18
H <sub>2</sub>	.74	.72	.74	.84	.97	.95
CO	1.08	1.00	.97	.96	1.02	1.02
S	1.18	1.05	.96	.73	.69	.72

## VII. LOW PRESSURE FLAMES

There have been several experimental studies of low pressure flames using mass spectroscopy. We consider one such experiment due to Fristrom, et al,<sup>27</sup> on a 7.85%  $\text{CH}_4/\text{O}_2$  flame at 0.05 atm pressure. The temperature,  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CH}_2\text{O}$  profiles were measured. The flame was stabilized on a circular screen burner. The experimental burning velocity (referenced to 298K, 0.05 atm) was 69 cm/sec.

The flame was modeled as an unbounded flame with the temperature of the unburned mixture as 298K. Computations were made using three kinetics schemes (CF20, W23, and DL18) and the more accurate transport Method VI. Since the flame is very lean, the  $\text{C}_2$  chemistry has only minor effects.

The temperature profiles were in very good agreement through the flame front. In the post flame region the experimental temperature measurements were high. For the major species  $\text{CH}_4$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ , all three models were in very good agreement with the experimental results. There were noticeable differences for the other species peak heights and the burning velocities (see Table 6). Dixon-Lewis<sup>4</sup> tried adjusting the rate constants to match the profiles. He was unable to do so and still match the atmospheric pressure experimental results.

Fristrom, et al, noted that recombination in the sampling probe could distort the trace species. To test this possibility, an ODE code was used. The initial temperature and concentrations were taken as the values at the peak  $\text{CH}_2\text{O}$  concentration, as determined by the CF20 model. A time integration was performed until the  $\text{CH}_2\text{O}$  concentration matched the experimental value, holding the temperature and pressure constant. The results are given in Table 4. The values for  $\text{H}_2$  and  $\text{CO}$  also closely match the experimental values. The major species concentrations also change, but since their concentrations are larger to begin with, this does not affect their agreement with the experimental profiles.

TABLE 6. A COMPARISON OF BURNING VELOCITIES AND PEAK MASS FRACTIONS FOR THE LOW PRESSURE FLAME

	Experiment	CF20	W23	DL18
Burning Velocity	69	55.7	62.1	39.5
$\text{CH}_2\text{O}$	1.5 E-3	3.1 E-3	1.1 E-3	1.2 E-3
$\text{H}_2$	2.2 E-4	2.3 E-4	1.3 E-4	9.0 E-5
$\text{CO}$	4.1 E-2	3.4 E-2	3.6 E-2	3.2 E-2

<sup>27</sup> R.M. Fristrom, C. Graefelder, and S. Favin, "Methane-Oxygen Flame Structure. III. Characteristic Profiles and Matter and Energy Conservation in a One-Twentieth Atmosphere Flame," *J. Phys. Chem.*, Vol. 65, pp. 587-590, 1961.

TABLE 7. RESULTS OF THE TIME INTEGRATION OF THE CF20 MODEL PROFILES.  
INITIAL CONDITIONS ARE TAKEN AT THE CH<sub>2</sub>O PEAK

	<u>t = 0</u>	<u>t = 3.2 E-4 sec</u>
CH <sub>2</sub> O	3.1 E-3	1.5 E-3
H <sub>2</sub>	2.3 E-4	2.2 E-4
CO	3.0 E-2	3.8 E-2

So it is possible that the differences between the CF20 model and the experiment are due to recombination within the probe. On the other hand, there is no obvious way recombination could lead to agreement between either the W23 or the DL18 scheme and the experiment. However, reactions on the wall of the probe and the cooling due to the probe have been ignored in this simple model. These assumptions cannot be justified, and the above explanation must be considered tentative.

#### VIII. CONCLUSIONS

Results for seven kinetic schemes have been compared with a range of data for atmospheric pressure methane/air flames. Three of the models (the two introduced here and the one due to Warnatz) are reasonably accurate over the entire range.

None of the models match the data on low pressure flame obtained by mass spectroscopy. However, if chemistry is assumed to continue for a short time in the probe, the predictions of the two new models are consistent with the experimental data.

None of the models can be considered to be completely validated. In particular, the CF14 models ignores C<sub>2</sub> chemistry, although it is known that C<sub>2</sub> species are formed. However, methane is oxidized in a series of steps. As long as the rate of the overall pathway is accurate, the flame speed, the temperature profiles, and the major species profiles will be accurate. But this does not guarantee that the intermediates CH<sub>3</sub>, CH<sub>2</sub>O, CHO, CH<sub>2</sub>, and the C<sub>2</sub> species will be correct.

A measurement of the CH<sub>3</sub> profile would be especially useful. This would help determine the branching ratio between CH<sub>3</sub> + CH<sub>2</sub>O and CH<sub>3</sub> + C<sub>2</sub>H<sub>6</sub>.

So there are several models that reproduce well the main features of atmospheric flame. Most of the models are accurate for lean to slightly rich flames. But the details of the intermediate reactions in the oxidation of CH<sub>4</sub> are still not well known.

#### ACKNOWLEDGEMENT

The author wishes to thank Dr. J.M. Heimerl for many helpful discussions.

## REFERENCES

1. L.D. Smoot, W.C. Hecker, and G.A. Williams, "Prediction of Propagating Methane-Air Flames," Combustion and Flame, Vol. 26, pp. 323-342, 1976.
2. G. Tsatsaronis, "Prediction of Propagating Laminar Flames in Methane, Oxygen, Nitrogen Mixtures," Combustion and Flame, Vol. 33, pp. 217-239, 1978.
3. J. Warnatz, "The Structure of Laminar Alkane-, Alkene-, and Acetylene Flames," 18th International Combustion Symposium, The Combustion Institute, Pittsburgh, PA, pp. 369-384, 1981.
4. G. Dixon-Lewis, "Aspects of the Kinetic Modeling of Methane Oxidation in Flames," 1st Specialists Meeting (International) of the Combustion Institute, France, pp. 284-289.
5. T.P. Coffee and J.M. Heimerl, "Transport Algorithms for Premixed, Laminar Steady-State Flames," Combustion and Flame, Vol. 43, pp. 273-289, 1981.
6. T.P. Coffee and J.M. Heimerl, "A Method for Computing the Flame Speed for a Laminar, Premixed, One Dimensional Flame," ARBRL-TR-02212, January 1980 (AD A082803).
7. J.M. Heimerl and T.P. Coffee, "The Detailed Modeling of Premixed, Laminar Steady-State Flames. I. Ozone," Combustion and Flame, Vol. 39, pp. 301-315, 1980.
8. T.P. Coffee, "A Computer Code for the Solution of the Equations Governing a Laminar, Premixed, One-Dimensional Flame," ARBRL-MR-03165, April 1982.
9. S. Gordon and B.J. McBride, "Computer Program for Calculation of Complex Chemical Equilibrium Compositions, Rocket Performance, Incident and Reflected Shocks and Chapman-Jouguet Detonations," NASA-SP-273, 1971 (1981 program version).
10. S. Benson, Thermochemical Kinetics, 2nd edition, John Wiley and Sons, NY, 1976.
11. R.C. Reed and J.K. Sherwood, The Properties of Gases and Liquids, 2nd edition, McGraw-Hill, NY, 1966.
12. R.A. Svehla, "Estimated Viscosities and Thermal Conductivities of Gases at High Temperatures," NASA Technical Report R-132, Lewis Research Center, Cleveland, OH, 1962.
13. G. Dixon-Lewis, "Kinetic Mechanism, Structure, and Properties of Premixed Flames in Hydrogen-Oxygen-Nitrogen Mixtures," Phil. Trans. Roy. Soc. (London), Vol. A292, pp. 45-99, 1979.
14. M.A. Cherian, P. Rhodes, R.J. Simpson, and G. Dixon-Lewis, "Structure, Chemical Mechanism and Properties of Premixed Flames in Mixtures of Carbon Monoxide, Nitrogen, and Oxygen with Hydrogen and Water Vapor," Phil. Trans. Roy. Soc. (London), Vol. A303, pp. 181-212, 1981.

15. A.M. Dean, R.L. Johnson, and D.C. Steiner, "Shock-Tube Studies of Formaldehyde Oxidation," Combustion and Flame, Vol. 37, pp. 41-62, 1980.
16. A.M. Dean and R.L. Johnson, "Shock Tube Studies of the  $N_2O/CH_4/CO/Ar$  and  $N_2O/C_2H_6/CO/Ar$  Systems," Combustion and Flame, Vol. 37, pp. 109-123, 1980.
17. R.J. Gelinas, "Ignition Kinetics of C1 and C2 Hydrocarbons," Science Applications, Inc., Preprint No. SAI/PL/C279, December 1979.
18. K. Luther and J. Troe, "Weak Collision Effects in Dissociation Reactions at High Temperatures," 17th International Combustion Symposium, The Combustion Institute, Pittsburgh, PA, pp. 535-542, 1979.
19. G.E. Andrews and D. Bradley, "Determination of Burning Velocities: A Critical Review," Combustion and Flame, Vol. 18, pp. 133-153, 1972.
20. G.E. Andrews and D. Bradley, "Determination of Burning Velocity by Double Ignition in a Closed Vessel," Combustion and Flame, Vol. 20, pp. 7-89, 1973.
21. R. Gunther and G. Janish, "Measurements of Burning Velocity in a Flat Flame Front," Combustion and Flame, Vol. 19, pp. 49-53, 1972.
22. R. Lindow, "Eine verbesserte Brennermethode zur Bestimmung der laminaren flammengeschwindigkeiten von Brenngas/Luft-Gemischen," Brennstoff Wärme Kraft, Vol. 20, pp. 8-14, 1968.
23. S.B. Reed, J. Mineur, and J.P. McNaughton, "The Effect on the Burning Velocity of Methane of Vitiation of Combustion Air," J. Inst. Fuel, Vol. 44, pp. 149-155, 1971.
24. J.H. Bechtel and R.E. Teets, "Hydroxyl and its Concentration Profile in Methane-Air Flames," Applied Optics, Vol. 18, pp. 4138-4144, 1979.
25. J.H. Bechtel, R.J. Blint, C.J. Dasch, and D.A. Weinberger, "Atmospheric Pressure Premixed Hydrocarbon-Air Flames: Theory and Experiment," Combustion and Flame, Vol. 42, pp. 197-213, 1981.
26. T.P. Coffee and J.M. Heimerl, "Sensitivity Analysis for Premixed Laminar, Steady-State Flames," Combustion and Flame, Vol. 50, pp. 323-340, 1983.
27. R.M. Fristrom, C. Crunfelder, and S. Favin, "Methane-Oxygen Flame Structure. III. Characteristic Profiles and Matter and Energy Conservation in a One-Twentieth Atmosphere Flame," J. Phys. Chem., Vol. 65, pp. 587-590, 1961.

# DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
12	Administrator Defense Technical Info Center ATTN: DTIC-DDA Cameron Station Alexandria, VA 22314	4	Commander US Army Research Office ATTN: R. Girardelli D. Mann R. Singleton D. Squire Research Triangle Park, NC 27709
1	Commander USA DARCOM ATTN: DRCMD-ST 5001 Eisenhower Avenue Alexandria, VA 22333	1	Commander USA Communications Research and Development Command ATTN: DRSEL-ATDD Fort Monmouth, NJ 07703
1	Commander USA AMCCOM ATTN: DRSMC-TDC(D) Dover, NJ 07801	1	Commander USA Electronics Research and Development Command Technical Support Activity ATTN: DELSD-L Fort Monmouth, NJ 07703
2	Commander USA AMCCOM ATTN: DRSMC-TSS(D) Dover, NJ 07801	2	Commander USA AMCCOM ATTN: DRSMC-LCA-G(D), D.S. Downs J.A. Lannon Dover, NJ 07801
1	Commander USA ARRCOM ATTN: DRSMC-LEP-L(R) Rock Island, IL 61299	1	Commander USA AMCCOM ATTN: DRSMC-LC(D), L. Harris Dover, NJ 07801
1	Director USA AMCCOM Benet Weapons Laboratory ATTN: DRSMC-LCB-TL(D) Watervliet, NY 12189	1	Commander USA AMCCOM ATTN: DRSMC-SCA-T(D), L. Stiefel Dover, NJ 07801
1	Commander USA Aviation Research and Development Command ATTN: DRDAV-E 4300 Goodfellow Blvd. St. Louis, MO 63120	1	Commander USA Missile Command ATTN: DRSMI-R Redstone Arsenal, AL 35898
1	Director USA Air Mobility Research and Development Laboratory Ames Research Center Moffett Field, CA 94035	1	Commander USA Missile Command ATTN: DRSMI-YDL Redstone Arsenal, AL 35898

# DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
2	Commander USA Missile Command ATTN: DRSMI-RK, D.J. Ifshin Redstone Arsenal, AL 35898	1	Commander Naval Surface Weapons Center ATTN: J.L. East, Jr., G-20 Dahlgren, VA 22448
1	Commander USA Tank Automotive Command ATTN: DRSTA-TSL Warren, MI 48090	1	Commander Naval Surface Weapons Center ATTN: G.B. Wilmot, R-16 Silver Spring, MD 20910
1	Director USA TRADOC Systems Analysis Activity ATTN: ATAA-SL WSMR, NM 88002	4	Commander Naval Weapons Center ATTN: R.L. Derr, Code 389 China Lake, CA 93555
2	Commandant US Army Infantry School ATTN: ATSH-CD-CSO-OR Fort Benning, GA 31905	1	Commander Naval Weapons Center ATTN: T. Boggs China Lake, CA 93555
1	Office of Naval Research Department of the Navy ATTN: R.S. Miller, Code 432 800 N. Quincy Street Arlington, VA 22217	1	Commander Naval Research Laboratory Washington, DC 20375
1	Navy Strategic Systems Project Office ATTN: R.D. Kinert, SP 2731 Washington, DC 20360	1	Commander US Naval Underwater Wpns Rsch & Engr Station ATTN: R.S. Lazar/Code 36301 Newport, RI 02840
1	Commander Naval Air Systems Command ATTN: J. Ramnarace, AIR-54111C Washington, DC 20360	1	Superintendent Naval Postgraduate School Dept. of Aeronautics ATTN: D.W. Netzer Monterey, CA 93940
3	Commander Naval Ordnance Station ATTN: C. Irish S. Mitchell P.L. Stang, Code 515 Indian Head, MD 20640	6	AFRPL (DRSC) ATTN: R. Geisler D. George B. Goshgarian J. Levine W. Roe D. Weaver Edwards AFB, CA 93523
		1	AFATL/DL DL ATTN: Dr. D. C. Daniel Eglin AFB, FL 32542

# DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
1	AFOSR ATTN: L.H. Caveny Bolling AFB, DC 20332	1	Battelle Memorial Institute Tactical Technology Center ATTN: J. Huggins 505 King Avenue Columbus, OH 43201
1	AFWL/SUL Kirtland AFB, NM 87117	2	Exxon Research & Eng. Co. ATTN: A. Dean M. Chou P.O. Box 8 Linden, NJ 07036
1	NASA Langley Research Center ATTN: G.B. Northam/MS 168 Hampton, VA 23365	1	Ford Aerospace and Communications Corp. DIVAD Division Div. Hq., Irvine ATTN: D. Williams Main Street & Ford Road Newport Beach, CA 92663
4	National Bureau of Standards ATTN: J. Hastie M. Jacox T. Kashiwagi H. Semerjian US Department of Commerce Washington, DC 20234	1	General Electric Armament & Electrical Systems ATTN: M.J. Bulman Lakeside Avenue Burlington, VT 05402
1	Aerojet Solid Propulsion Co. ATTN: P. Micheli Sacramento, CA 95813	1	General Electric Company ATTN: M. Lapp Schenectady, NY 12305
1	Applied Combustion Technology, Inc. ATTN: A.M. Varney P.O. Box 17885 Orlando, FL 32860	1	General Electric Ordnance Systems ATTN: J. Mandzy 100 Plastics Avenue Pittsfield, MA 01203
2	Atlantic Research Corp. ATTN: M.K. King 5390 Cherokee Avenue Alexandria, VA 22314	1	General Motors Rsch Labs Physics Department ATTN: J.H. Bechtel Warren, MI 48090
1	Atlantic Research Corp. ATTN: R.H.W. Waesche 7511 Wellington Road Gainesville, VA 22065	3	Hercules Powder Co. Alleghany Ballistics Lab. ATTN: R.R. Miller P.O. Box 210 Cumberland, MD 21501
1	AVCO Everett Rsch. Lab. Div. ATTN: D. Stickler 2385 Revere Beach Parkway Everett, MA 02149		

# DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
3	Hercules, Inc. Bacchus Works ATTN: K.P. McCarty P.O. Box 98 Magna, UT 84044	1	Paul Gough Associates, Inc. ATTN: P.S. Gough 1048 South Street Portsmouth, NH 03801
1	Hercules, Inc. AFATL/DL DL ATTN: R.L. Simmons Eglin AFB, FL 32542	2	Princeton Combustion Research Laboratories ATTN: M. Summerfield N.A. Messina 1041 US Highway One North Princeton, NJ 08540
1	Honeywell, Inc. Gov't & Aerospace Products Div ATTN: D.E. Broden/ MS MN50-2000 600 2nd Street NE Hopkins, MN 55343	1	Hughes Aircraft Company ATTN: T.E. Ward 8433 Fallbrook Avenue Canoga Park, CA 91303
1	IBM Corporation ATTN: A.C. Tam Research Division 5600 Cottle Road San Jose, CA 95193	1	Rockwell International Corp. Rocketdyne Division ATTN: J.E. Flanagan/HB02 6633 Canoga Avenue Canoga Park, CA 91304
1	Director Lawrence Livermore Lab ATTN: C. Westbrook P.O. Box 808 Livermore, CA 94550	2	Sandia National Laboratories Combustion Sciences Dept. ATTN: R. Cattolica D. Stephenson Albuquerque, NM 87115
1	Lockheed Missiles & Space Co. ATTN: George Lo 3251 Hanover Street Dept. 52-35/B204/2 Palo Alto, CA 94304	1	Science Applications, Inc. ATTN: R.B. Edelman 23146 Cumorah Crest Woodland Hills, CA 91364
1	Los Alamos Scientific Lab ATTN: B. Nichols T7, MS-B284 P.O. Box 1663 Los Alamos, NM 87545	1	Science Applications, Inc. ATTN: H.S. Pergament 1100 State Road, Bldg. N Princeton, NJ 08540
1	Olin Corporation Smokeless Powder Operations ATTN: R.L. Cook P.O. Box 222 St. Marks, FL 32355	1	Space Sciences, Inc. ATTN: M. Farber Monrovia, CA 91016

# DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
4	SRI International ATTN: S. Barker D. Crosley D. Golden Tech Lib 333 Ravenswood Avenue Menlo Park, CA 94025	1	Universal Propulsion Company ATTN: H.J. McSpadden Black Canyon Stage 1 Box 1140 Phoenix, AZ 85029
1	Stevens Institute of Tech. Davidson Laboratory ATTN: R. McAlevy, III Hoboken, NJ 07030	1	Veritay Technology, Inc. ATTN: E.B. Fisher P.O. Box 22 Bowmansville, NY 14026
1	Teledyne McCormack-Selph ATTN: C. Leveritt 3601 Union Road Hollister, CA 95023	1	Brigham Young University Dept. of Chemical Engineering ATTN: M.W. Beckstead Provo, UT 84601
1	Thiokol Corporation Elkton Division ATTN: W.N. Brundige P.O. Box 241 Elkton, MD 21921	1	California Institute of Tech. Jet Propulsion Laboratory ATTN: MS 125/159 4800 Oak Grove Drive Pasadena, CA 91102
3	Thiokol Corporation Huntsville Division ATTN: D.A. Flanagan Huntsville, AL 35807	1	California Institute of Technology ATTN: F.E.C. Culick/ MC 301-46 204 Karman Lab. Pasadena, CA 91102
3	Thiokol Corporation Wasatch Division ATTN: J.A. Peterson P.O. Box 524 Brigham City, UT 84302	1	University of California, Berkeley Mechanical Engineering Dept. ATTN: J. Daily Berkeley, CA 94720
1	United Technologies ATTN: A.C. Eckbreth East Hartford, CT 06108	1	University of California Los Alamos Scientific Lab ATTN: T.D. Butler P.O. Box 1663, Mail Stop B216 Los Alamos, NM 87545
2	United Technologies Corp. ATTN: R.S. Brown R.O. McLaren P.O. Box 358 Sunnyvale, CA 94086	2	University of California, Santa Barbara Quantum Institute ATTN: K. Schofield M. Steinberg Santa Barbara, CA 93106

# DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
1	University of Southern California Dept. of Chemistry ATTN: S. Benson Los Angeles, CA 90007	1	University of Illinois Dept. of Mech. Eng. ATTN: H. Krier 144MEB, 1206 W. Green St. Urbana, IL 61801
1	Case Western Reserve Univ. Div. of Aerospace Sciences ATTN: J. Tien Cleveland, OH 44135	1	Johns Hopkins University/APL Chemical Propulsion Information Agency ATTN: T.W. Christian Johns Hopkins Road Laurel, MD 20707
1	Cornell University Department of Chemistry ATTN: E. Grant Baker Laboratory Ithaca, NY 14850	1	University of Minnesota Dept. of Mechanical Engineering ATTN: E. Fletcher Minneapolis, MN 55455
1	Univ. of Dayton Rsch Inst. ATTN: D. Campbell AFRPL/PAP Stop 24 Edwards AFB, CA 93523	4	Pennsylvania State University Applied Research Laboratory ATTN: G.M. Faeth K.K. Kuo H. Palmer M. Micci University Park, PA 16802
1	University of Florida Dept. of Chemistry ATTN: J. Winefordner Gainesville, FL 32601	1	Polytechnic Institute of NY ATTN: S. Lederman Route 110 Farmingdale, NY 11735
1	Georgia Institute of Technology School of Aerospace Engineering ATTN: E. Price Atlanta, GA 30332	2	Princeton University Forrestal Campus Library ATTN: K. Brezinsky I. Glassman P.O. Box 710 Princeton, NJ 08540
2	Georgia Institute of Technology School of Aerospace Engineering ATTN: W.C. Strahle B.T. Zinn Atlanta, GA 30332	1	Princeton University MAE Dept. ATTN: F.A. Williams Princeton, NJ 08544

# DISTRIBUTION LIST

<u>No. Of Copies</u>	<u>Organization</u>	<u>No. Of Copies</u>	<u>Organization</u>
2	Purdue University School of Aeronautics and Astronautics ATTN: R. Glick J.R. Osborn Grissom Hall West Lafayette, IN 47906	1	Stanford University Dept. of Mechanical Engineering ATTN: R. Hanson Stanford, CA 94305
3	Purdue University School of Mechanical Engineering ATTN: N.M. Laurendeau S.N.B. Murthy D. Sweeney TSPC Chaffee Hall West Lafayette, IN 47906	2	University of Texas Dept. of Chemistry ATTN: W. Gardiner H. Schaefer Austin, TX 78712
1	Rensselaer Polytechnic Inst. Dept. of Chemical Engineering ATTN: A. Fontijn Troy, NY 12181	1	University of Utah Dept. of Chemical Engineering ATTN: G. Flandro Salt Lake City, UT 84112
2	Southwest Research Institute ATTN: R.E. White A.B. Wenzel 8500 Culebra Road San Antonio, TX 78228	1	Virginia Polytechnic Institute and State University ATTN: J.A. Schetz Blacksburg, VA 24061
			<u>Aberdeen Proving Ground</u>
			Dir, USAMSAA ATTN: DRXSY-D DRXSY-MP, H. Cohen Cdr, USATECOM ATTN: DRSTE-TO-F Cdr, CRDC, USA AMCCOM ATTN: DRSMC-CLB-PA DRSMC-CLN DRSMC-CLJ-L

### USER EVALUATION OF REPORT

Please take a few minutes to answer the questions below; tear out this sheet, fold as indicated, staple or tape closed, and place in the mail. Your comments will provide us with information for improving future reports.

1. BRL Report Number \_\_\_\_\_

2. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which report will be used.)  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

3. How, specifically, is the report being used? (Information source, design data or procedure, management procedure, source of ideas, etc.) \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

4. Has the information in this report led to any quantitative savings as far as man-hours/contract dollars saved, operating costs avoided, efficiencies achieved, etc.? If so, please elaborate.  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

5. General Comments (Indicate what you think should be changed to make this report and future reports of this type more responsive to your needs, more usable, improve readability, etc.) \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

6. If you would like to be contacted by the personnel who prepared this report to raise specific questions or discuss the topic, please fill in the following information.

Name: \_\_\_\_\_

Telephone Number: \_\_\_\_\_

Organization Address: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_

----- FOLD HERE -----

Director  
US Army Ballistic Research Laboratory  
ATTN: DRSMC-BLA-S (A)  
Aberdeen Proving Ground, MD 21005

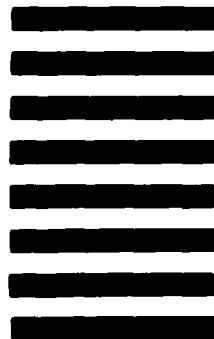


NO POSTAGE  
NECESSARY  
IF MAILED  
IN THE  
UNITED STATES

OFFICIAL BUSINESS  
PENALTY FOR PRIVATE USE, \$300



Director  
US Army Ballistic Research Laboratory  
ATTN: DRSMC-BLA-S (A)  
Aberdeen Proving Ground, MD 21005



----- FOLD HERE -----